

PATENT SPECIFICATION

NO DRAWINGS

Bulk polymerization
1,141,165

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COMPLETE SPECIFICATION

Process for the Manufacture of Acrylic Films

We, FIRMA ASCHAFFENBURGER ZELLSTOFFWERKE AKTIENGESELLSCHAFT, a joint stock company organised under the laws of Germany, of Redenfelden/Obb. Germany, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the production of acrylic polymers, with the special purpose of manufacturing plastic films.

The usual method for manufacturing plastic films consists in the extrusion of polymers or precipitation from polymeric solutions and subsequent stretching of the film formed. By means of the so-called bulk polymerization, polymers with a particularly smooth and non-porous surface are obtained.

It is known that acrylic and methacrylic acid ester polymers are—depending on their chemical composition—hard, elastic or plastic materials. It is further known that the elasticity of polymers can be improved by so-called internal plasticizers, e.g. by copolymerization of methacrylic acid methyl ester with esters of acrylic acid having short-chain alkyl groups (C₁ to C₂). While the elasticity of products thus obtained is sufficient for inherently stable materials of a thickness of approximately 0.5 mm and more, it is insufficient for the manufacturing of films which have to withstand a considerably higher elastic strain.

Furthermore, it is known that the polymerization of methacrylic acid methyl ester and its homologues, as well as the polymerization of acrylic acid alkyl esters, in the presence of phosphoric acid anhydride and alcohols result in flameproof films, the phosphoric acid anhydride and alcohol con-

densation product acting as an external plasticizer which does not take part in the 45 polymerization reaction.

It is further known that by two-dimensional or three-dimensional cross-linking the swelling properties and the solubility of such products can be reduced ad libitum, 50 whereby the dimensional stability under heat and the hardness of the polymers are increased.

According to the present invention there is provided a process for manufacturing 55 acrylic films, wherein a methacrylic acid alkyl ester having 1 to 4 carbon atoms in the alkyl group (A), in an amount between 50% and 90%, is reacted by freed radical bulk polymerization, with an acrylic acid 60 ester (B) in an amount between 5% and 40% and with 5% to 45% of an ester of a polyethoxylated product containing at least one acrylic or methacrylic acid ester-group and optionally an ester group derived from 65 another aliphatic or aromatic mono- or dicarboxylic acid (C), the percentages being by weight and based on the total weight of the monomers, and the reaction being carried out between two shaping members 70 to produce a film.

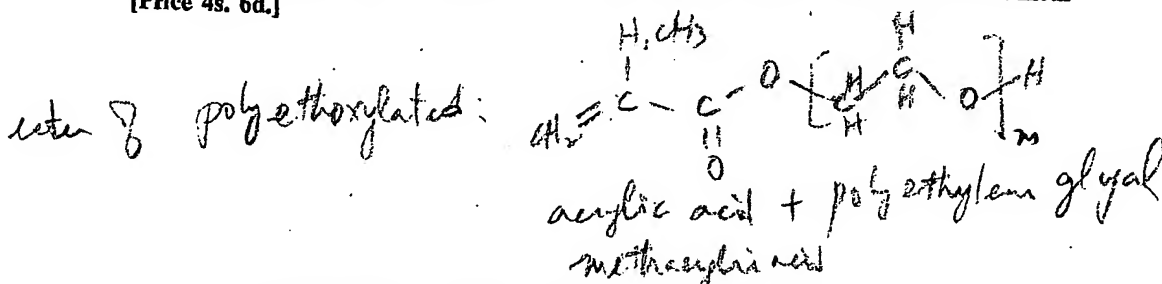
It is to be understood that the acrylic ester (B) does not include the esters of a polyethoxylated product as defined for (C).

The acrylic ester (B) may be an alkyl (C₁ to C₂), alkoxyalkyl, hydroxyalkyl, haloalkyl, epoxyalkyl, aryl, arylalkyl, or alkyaryl acrylate. A preferred material is an acrylic n-butyl ester present in an amount of between 10% and 20% by weight.

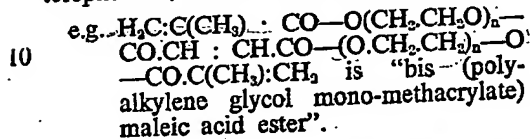
The acrylic monomer (A) is preferably methacrylic acid methyl ester.

Component (C) is preferably present in an amount of 15% to 25% and may be a dimethacrylic or diacrylic acid ester of a 85 polyalkylene glycol. Instead of the dimeth-

[Price 4s. 6d.]



acrylic or diacrylic acid esters of polyalkylene glycols, it is possible to use the following mixed esters; mono-methacrylic or acrylic acid-monomerpropionic or -butyric or -stearic acid ester of polyalkylene glycols, or bis-(polyalkyleneglycol mono-methacrylate or acrylate) esters of maleic, phthalic, terephthalic, fumaric, or itaconic acid:



It is advantageous to use the mixed esters of the poly-ethoxylated compounds derived from both saturated and unsaturated aliphatic or aromatic mono- and/or dicarboxylic acids.

The polymerization is carried out in the usual manner by moulding, preferably between glass plates or inert metal foils or plastic foils, with addition of the usual free radical catalysts, and, if necessary, of accelerators or activators with or without heat supply.

The process may include the step of prepolymerizing two or more of the monomer reactants.

The polymer films produced can easily be stripped from the supports, e.g. plates or foils, particularly in the case when component (C) is a methacrylic or acrylic acid ester of a polyethoxylated alkylphenol.

The acrylic polymer films produced in this way show, depending on their composition, good properties in respect of tensile strength, bursting strength, workability and transparency.

The invention is illustrated by the following Examples, where all parts and percentages referred to are by weight, unless otherwise stated.

EXAMPLE I

69.7 parts methacrylic acid methyl ester, 10.0 parts acrylic acid n-butyl ester and 20.0 parts of the dimethacrylic acid ester of polyethyleneglycol (M.Wt 600) were prepolymerized to syrup consistency with 0.03 parts azodiisobutyronitrile. After cooling 0.3 parts crosslinking agent (the dimethacrylic acid ester of triethylene glycol) and polymerization catalyst comprising 2.0 parts permaleic acid tertiary butyl ester (paste-50% plasticizer), 1.6 parts lauryl mercaptan, 1.0 part activator solution, (40% benzyl dimethyl laurylammoniumchloride, 0.217% CuCl_2 and balance ethyl alcohol) were added.

This mixture was poured after de-aeration on to a flat inert supporting film, covered with a second film, and after adjusting the thickness by pressing with a roll, it was polymerized at 50°C to a flexible tenacious colourless film.

EXAMPLE II

57.5 parts methacrylic acid methyl ester, 20.0 parts acrylic acid n-butyl ester, 20.0 parts mixed methacrylic acid-propionic acid ester of polyethylene glycol (M.Wt 600) and 2.0 parts methacrylic acid ester of a polyethoxylated nonyl phenol were prepolymerized to syrup consistency with 0.03 parts azodiisobutyronitrile. After cooling, 0.5 parts crosslinking agent (the dimethacrylic acid ester of triethylene glycol) and the polymerization catalyst consisting of 0.5 parts permaleic acid tertiary butyl ester (paste-50% plasticizer) and 0.5 parts activator (1 molar proportion of ZnO and 2 molar proportions of thioglycolic acid 2-ethyl-hexyl ester) were added. The mixture was de-aerated by vacuum, pressed with a roll between supporting films and polymerised at 55°C. A highly elastic colourless film with high water vapour permeability was obtained.

WHAT WE CLAIM IS:-

1. Process for manufacturing acrylic films, wherein a methacrylic acid alkyl ester having 1 to 4 carbon atoms in the alkyl group (A), in an amount between 50% and 90%, is reacted by free radical bulk polymerization, with an acrylic acid ester (B) in an amount between 5% and 40%, and with 5% to 45% of an ester of a polyethoxylated product containing at least one acrylic or methacrylic acid ester group and optionally an ester group derived from another aliphatic or aromatic mono- or dicarboxylic acid (C), the percentages being by weight and based on the total weight of the monomers, and the reaction being carried out between two shaping members to produce a film.

2. Process according to claim 1, wherein the monomer (A) is methacrylic acid methyl ester.

3. Process according to claim 1, wherein the acrylic acid ester (B) is an alkyl (C_1 to C_{10}), alkoxyalkyl, hydroxyalkyl, haloalkyl, epoxyalkyl, aryl, arylalkyl, or alkylaryl acrylate.

4. Process according to any preceding claim, wherein the acrylic acid ester (B) is acrylic acid n-butyl ester and is present in an amount of between 10% and 20% by weight.

5. Process according to any preceding claim, wherein the ester (C) is a dimethacrylic acid ester or monomethacrylic acid-monomerpropionic ester of polyethylene glycol and is present in an amount of between 15% and 25% by weight.

6. Process as claimed in any preceding claim, which includes the step of prepolymerizing two or more of the monomer reactants.

7. Process for manufacturing acrylic

films as claimed in claim 1 and substantially as hereinbefore described with reference to either of the Examples.

8. Acrylic films whenever prepared or
5 produced by a process claimed in any of the preceding claims.

MATHISEN & MACARA,
Chartered Patent Agents,
Lyon House,
Lyon Road,
Harrow,
Middlesex.
Agents for the Applicants.

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